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Tetrachlorodibenzodioxin Isomer Differentiation by Micro Diffuse Reflectance Fourier Transform Infrared Spectrometry at the Low Nanogram Level

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16. ABSTRACT

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Tetrachlorodibenzodioxin Isomer Differentiation by Micro Diffuse Reflectance Fourier Transform Infrared Spectrometry at the Low Nanogram Level

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Infrared diffuse reflectance spectra were recorded for the 22 tetrachlorodibenzodioxin isomers (TCDDs). By use of micro-DRIFT techniques and signal averaging, identifiable spectra for each of the isomers were achieved at low nanogram levels. Spectral features in the 1200 cm^{-1} to 1600 cm^{-1} region indicate that each isomer has a unique spectrum and is readily distinguishable from other isomeric TCDDs. Each TCDD isomer was correctly identified, from a user-created library of the 22 isomers, using a software algorithm. The uniqueness of the TCDD FT-IR spectra offers the previously unobtainable possibility of correct isomer identification, in the presence of isomeric chromatographic coelution interferences, by spectral subtraction. These DRIFT spectra were utilized to clarify ambiguous TCDD structural assignments. Utilization of these FT-IR techniques for environmental monitoring can complement the current procedure of gas chromatography/mass spectrometry (GC/MS) for dioxin characterization.

One of the most difficult analytical problems currently facing environmental analysis is the differentiation and quantification of the isomeric tetrachlorodibenzodioxins (TCDDs). For recent reviews on TCDD analysis see ref 1–3. Since TCDD toxicity is strongly isomer dependent (*4*), isomer differentiation is critical to meaningful dioxin analysis. Past approaches to analysis include both low (*5*, *6*) and high (*7*) resolution GC/MS, negative ion chemical ionization GC/MS (*8*, *9*) and electron capture gas chromatography (*10*). Although these techniques have been used to routinely produce quantitative data in the low parts-per-billion range, and under certain conditions in the parts-per-trillion range, none offer an isomer specific technique which is independent of chromatographic separation. Some isomer specificity has been demonstrated by Mitchum et al. using oxygen negative ion chemical ionization (*11*) atmospheric pressure mass spectrometry to monitor the products of the unique oxygen initated reaction with TCDD (*12*, *13*). This methodology allowed the separation of the TCDDs into three distinct groups (0:4, 1:3, 2:2, where the colon separated numbers indicate the number of chlorines in each aromatic ring) but unambiguous structural assignments of the isomers within each group could not be made.

Separation of each TCDD isomer from the 21 other isomers has not yet been reported using a single gas chromatographic column although separation of the 2,3,7,8 isomer can be achieved. Certain isomer pairs, notably the 1,2,4,6-/1,2,4,9-TCDD and 1,2,4,7-/1,2,4,8-TCDD isomers have not been completely resolved using gas chromatography techniques. Furthermore, the order of elution of the TCDD isomers as reported by Buser (*14*) differs from the elution order reported by workers at Dow (*15*) resulting in some ambiguity in the chlorine isomer assignment of certain of these isomers. Those isomers whose identity is in question include 1,2,6,8-, 1,2,7,8-, and 1,2,7,9-TCDD. Assignment of structure for each of these isomers, as well as others which are difficult to resolve chromatographically, is proposed based on interpretation of the diffuse reflectance infrared Fourier transform (DRIFT) spectra obtained in this study. Information regarding the precise identification of these isomers is important in the development of new and improved analytical techniques for the analysis of dioxin at low levels in environmental samples.

Although isomer differentiation is the natural domain of infrared techniques, the extra sensitivity of the IR method resulting from interferometric and Fourier transform infrared (FT-IR) techniques has not been sufficient to achieve sub-nanogram sensitivities for on-line environmental monitoring (*16–18*). However, Cournoyer reported low nanogram FT-IR sensitivities using off-line micropelleting techniques and multihour signal averaging (*19*) while Griffiths and Fuller had reported low nanogram sensitivities for off-line micro-DRIFT techniques (*20*, *21*). Chen achieved microgram sensitivities using a microsampling, grating IR technique for 24 chlorinated dibenzodioxins including three TCDDs (*22*). Successful utilization of the isomer differentiation capability of the IR and FT-IR techniques for environmental analysis required further sensitivity improvements and the availability of suitable on-line separation techniques.

The DRIFT method is a logical choice for isomer differentiation at nanogram levels. The problems associated with preparing DRIFT samples have been summarized by Griffiths et al. (*23*, *24*) and Azarraga et al. (*25*). Nyquist (*26*) has utilized Drift to differentiate the environmentally important pentachlorobiphenyl isomers. The technique has been shown to be applicable to high-performance liquid chromatography (HPLC) FT-IR (*27*, *28*) and supercritical fluid chromatography (SCF) FT-IR (*29*, *30*). DRIFT employs a static sampling mode; thus the spectral signal-to-noise (S/N) may be improved by extensive interferogram coaddition.

EXPERIMENTAL SECTION

DRIFT Instrumentation. A Digilab (Cambridge, MA) Model FTS-10 Fourier transform infrared spectrometer equipped with a broad band mercury–cadmium–telluride (MCT) detector was used for all DRIFT measurements. The spectrometer was continually purged with dry nitrogen gas. DRIFT measurements were performed with a modified (Ossining, NY) Harrick "praying mantis" diffuse reflectance (DR) accessory. This accessory was modified to employ a 1 mm diameter rod with a cupped end capable of holding a 0.5–1.0 mm potassium bromide disk. DRIFT spectra were measured at 4 cm^{-1} resolution by the coaddition of 1000 FT-IR scans. A background spectrum of each sample rod was obtained prior to sample deposition and subsequently subtracted from the sample spectrum.

Isomer Preparation. The TCDD isomers were prepared for the US EPA by the Wright State University (Cooperative

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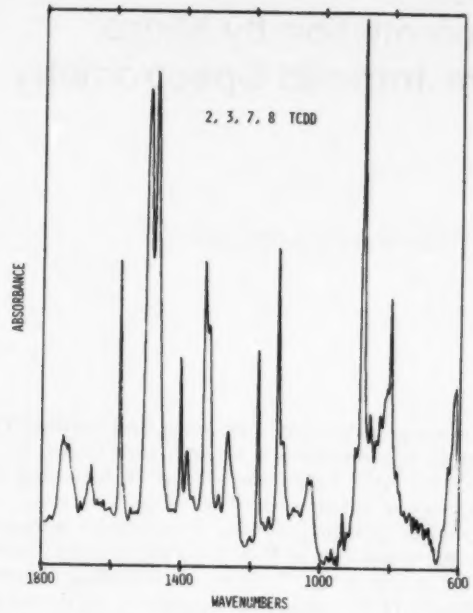

Figure 1. DRIFT spectrum of 2,3,7,8-TCDD.

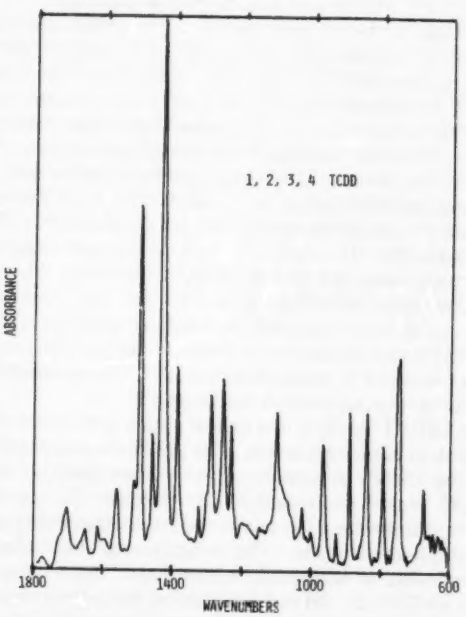

Figure 2. DRIFT spectrum of 1,2,3,4-TCDD.

Agreement No. CR 809972-01-0). The synthesis was accomplished by reaction of the alkali metal salt of a chlorinated catechol with the selected chlorinated benzene. The dioxins formed during this synthesis were separated from the residual starting materials and reaction byproducts using HPLC techniques. Some of these isomers may be purchased from Cambridge Isotope Laboratories, Woburn, MA.

DRIFT Sampling. Hexane solutions of the TCDD isomers were condensed, using a heat lamp, to yield about 10 μL of solution. About 2 μL of solution (50 to 200 ng of TCDD) was deposited on a micro KBR pellet which was inserted in the cupped tip of a 1-mm metal rod. Slightly translucent KBR pellets were prepared using less than 1 mm of KBR in a 13 mm die.

RESULTS AND DISCUSSION

The DRIFT spectra recorded for some of the TCDD isomers are presented in Figures 1–3 in absorbance units. The figures show the spectral region between 600 and 1800 cm^{-1}. The

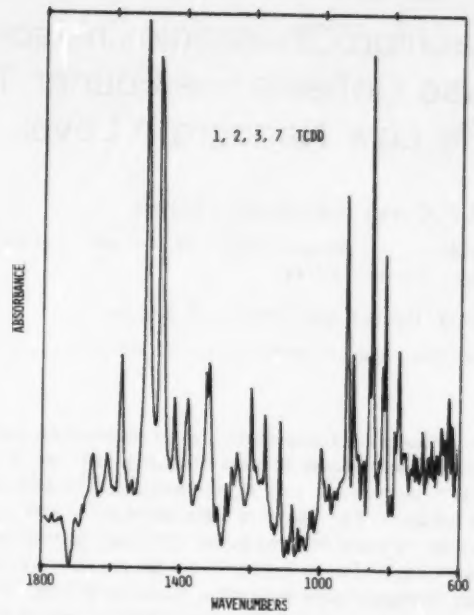

Figure 3. DRIFT spectrum of 1,2,3,7-TCDD.

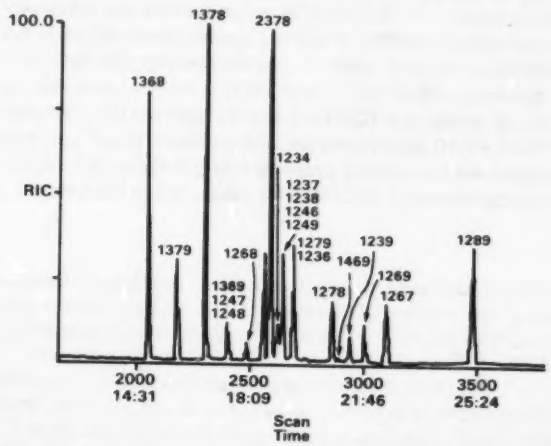

Figure 4. Total ion chromatogram of the 22 TCDD isomers chromatographed on a 50-m SIL-88 fused silica capillary column.

region beyond 1800–4000 cm^{-1} is clear of any absorption features except for weak C–H aromatic stretch bands around 3100 cm^{-1}. It is apparent that under these conditions high signal-to-noise spectra are obtainable for 50–200 ng of these isomers. The major spectral bands for the isomers are listed in Table I. The most intense band for all isomers was in the 1423–1491 cm^{-1} spectral region suggesting that TCDD isomers may be differentiated by this band.

The ability of the DRIFT technique to differentiate among the TCDD isomers was tested by creating a user library of isomer spectra and searching each isomer against the library. The library spectra were compressed into only three spectral regions. Each isomer was correctly identified by this algorithm.

A total ion chromatogram obtained for the 22 TCDD isomers on a 50-m CP SIL-88 fused silica capillary column is given in Figure 4. The elution order assignments in this figure are based upon Battelle Columbus unpublished work and previously reported TCDD elution orders. These measurements were performed with high-resolution gas chromatography in combination with low-resolution mass spectrometry. The mass spectrometer (MS) was not able to distinguish each

Table I. DRIFT Band Positions for TCDD Isomers

TCDD isomer	DRIFT bands, cm^{-1}
2,3,7,8	1570, 1489, *1470*[a], 1396, 1377, 1329, 1315, 1261, 1173, 1117, 1103, 1030, 1018, 872, 851, 835, 822, 801, 791, 733
1,2,3,6	1570, 1477, *1450*, 1310, 1288, 1263, 1155, 1142, 1072, 1024, 993, 961, 843, 802, 768, 704
1,2,3,8	1568, 1489, *1454*, 1420, 1381, 1325, 1315, 1296, 1263, 1234, 1198, 1159, 1113, 1082, 1016, 939, 860, 835, 804
1,2,8,9	1580, *1477*, 1460, 1435, 1418, 1381, 1339, 1306, 1261, 1198, 1179, 1167, 1140, 1113, 1103, 1086, 1020, 961, 949, 935, 800
1,2,3,7	1570, *1497*, 1460, 1420, 1379, 1327, 1319, 1198, 1157, 1115, 922, 905, 858, 849, 820, 810, 785, 772
1,3,6,8	1578, *1476*, 1418, 1302, 1261, 1236, 1227, 1196, 1177, 1084, 1047, 1040, 1020, 980, 858, 847, 829, 727, 704
1,2,6,7	1576, *1462*, 1385, 1350, 1310, 1198, 968, 907, 802
1,2,6,9	1599, 1574, 1553, 1530, 1510, 1503, *1468*, 1450, 1423, 1379, 1356, 1342, 1331, 1296, 1263, 1198, 1188, 1163, 1136, 1123, 1101, 1055, 1036, 1020, 999, 966, 949, 937, 916, 907, 891, 883, 835, 804, 797, 773, 758, 748, 700
1,4,7,8	1572, 1553, 1530, 1491, 1464, *1449*, 1416, 1395, 1379, 1358, 1300, 1261, 1175, 1159, 1128, 1113, 1074, 1049, 1042, 1030, 972, 947, 932, 905, 895, 872, 854, 843, 826, 810, 793, 770, 750, 725, 706
1,2,3,4	1599, 1564, 1539, 1512, 1497, 1462, *1433*, 1391, 1362, 1344, 1327, 1292, 1258, 1234, 1204, 1196, 1186, 1152, 1125, 1101, 1030, 1003, 986, 968, 939, 930, 908, 891, 868, 841, 818, 795, 777, 746, 708
1,3,7,8	1574, 1558, 1539, 1523, 1506, 1489, *1476*, 1449, 1437, 1418, 1381, 1364, 1346, 1310, 1261, 1186, 1163, 1117, 1086, 1042, 1018, 982, 949, 926, 918, 895, 872, 841, 812, 781, 772, 752, 702
1,2,7,9	1601, 1574, 1491, *1466*, 1429, 1379, 1323, 1312, 1291, 1261, 1233, 1221, 1200, 1179, 1161, 1113, 1076, 1061, 1045, 1024, 1016, 978, 941, 908, 895, 872, 847, 800, 779, 764, 745
1,2,6,8	1576, 1483, *1468*, 1431, 1308, 1261, 1198, 970, 949, 912, 843, 804
1,2,3,9	1597, 1570, 1539, 1506, 1477, 1462, *1452*, 1427, 1408, 1398, 1385, 1310, 1265, 1223, 1194, 1157, 935, 920, 856, 800, 700
1,2,7,8	1477, *1466*, 1306, 1263, 984, 837, 804, 797
1,3,6,9	1576, 1476, 1462, *1449*, 1431, 1412, 1385, 1354, 1331, 1321, 1304, 1290, 1273, 1254, 1221, 1196, 1161, 1113, 1084, 1071, 1047, 1036, 1023, 1015, 976, 943, 934, 926, 889, 847, 822, 795, 781, 754, 731, 721, 700
1,4,6,9	1570, 1541, 1524, 1506, 1472, *1460*, 1408, 1379, 1350, 1342, 1329, 1285, 1263, 1227, 1211, 1192, 1140, 1117, 1092, 1078, 1065, 1040, 1020, 972, 955, 935, 893, 883, 866, 839, 802, 770, 756, 745, 733, 721, 705
1,3,7,9	1572, 1535, 1514, *1483*, 1440, 1420, 1406, 1381, 1362, 1304, 1261, 1223, 1211, 1198, 1167, 1138, 1120, 1105, 1084, 1074, 1043, 1032, 1018, 997, 984, 974, 955, 941, 883, 870, 843, 812, 799, 791, 766, 745, 735, 718, 700
1,2,4,6	1576, 1560, 1539, 1520, 1504, 1479, *1464*, 1456, 1416, 1381, 1356, 1339, 1331, 1314, 1290, 1256, 1242, 1223, 1207, 1173, 1161, 1132, 1121, 1094, 1084, 1070, 1059, 1049, 1024, 1013, 974, 924, 912, 905, 887, 843, 785, 770, 746, 702
1,2,4,9	1574, 1560, *1474*, 1445, 1418, 1381, 1290, 1261, 1240, 1204, 1179, 1161, 1140, 1101, 1070, 1059, 1042, 1016, 1009, 980, 957, 930, 845, 772, 700
1,2,4,7	1595, 1576, 1539, 1491, 1460, 1445, *1423*, 1408, 1381, 1354, 1290, 1271, 1229, 1215, 1202, 1194, 1165, 1150, 1115, 1097, 1080, 1057, 1047, 1040, 1024, 972, 962, 934, 914, 881, 872, 862, 841, 806, 789, 762, 752, 727, 716
1,2,4,8	1493, *1456*, 1425, 1410, 1288, 1263, 1113, 1074, 1053, 1032, 978, 853, 816, 802

[a] Frequency in italics indicates the most intense spectral band.

of the individual isomers. Instead, this identification is based on matching chromatographic retention times of sample components with those of reference standards available from other sources.

Sensitivity. To ascertain the TCDD sensitivity limits for the DRIFT method, samples were prepared which contained 10 and 50 ng of the 1,3,7,8-TCDD isomer. Characteristic spectra were obtained for both concentration levels with an intense band at 1480 cm^{-1} readily observable at 10 ng with a S/N ratio indicating that subnanogram measurements are possible. This also suggests that using a more sensitive, narrow band MCT detector (cutoff at 800 cm^{-1}) and/or increasing the FT-IR signal averaging time would lead to subnanogram TCDD DRIFT sensitivity levels. The broad band MCT detector used in this study is unnecessary, since the TCDD isomers are mutually distinguishable by use of the information obtained at spectral frequencies higher than 800 cm^{-1}. Twenty of the isomers can be unambiguously assigned on the basis of the intense bands between 1500 and 1400 cm^{-1} and the remaining two require confirmation from an equally strong band at 900 cm^{-1}. Since the most intense bands are in a common spectral region, these sensitivity limits for the 1,3,7,8 isomer should apply to all the isomers. However, it should be understood that these sensitivity limits may be strongly affected by interfering background constituents in the sample extract.

TCDD Isomer Assignment by IR Spectra. Measurements of infrared spectra have been shown to provide a means to unambiguously identify the isomers of TCDD. Twenty can be assigned solely on the basis of the strong bands between 1500 and 1400 cm^{-1}, and the other two require only one other band for discrimination. This fact may be simply demonstrated by overlaying transparencies of the spectra.

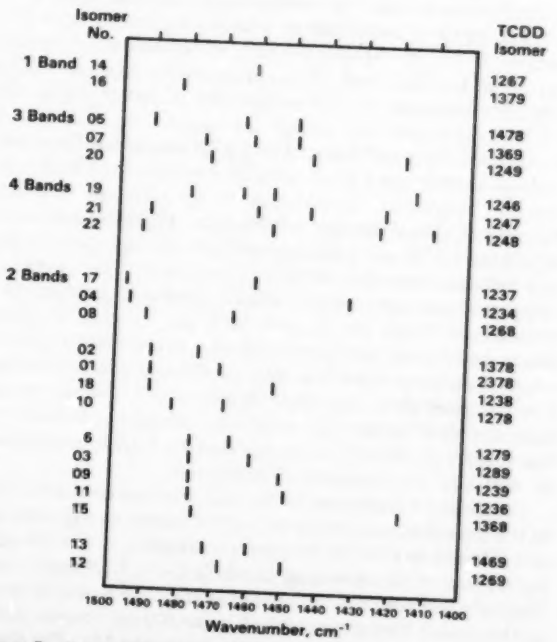

Figure 5. Spectral bar graph for the TCDD isomers.

The discriminating ability of this technique can also be shown by the bar graph, Figure 5, showing only the bands in the 1500–1400 cm^{-1} region. The spectra of the 22 isomers can be classified into four groups based on the number of well-resolved bands in that region. Only in the case of 1,2,3,9-TCDD and 1,2,3,6-TCDD is there sufficient coincidence to

Table II. DRIFT Assignments for Ambiguous TCDD Isomer Solutions

compound no.	DRIFT assignment	original assignment(s)	basis for assignment
6	1,2,7,9	1,2,7,9 (1,2,6,8)	*a*
8	1,2,6,8	1,2,7,8 (1,2,6,8)	*a*
10	1,2,7,8	1,2,7,8 (1,2,7,9)	*a*
19	1,2,4,6	1,2,4,6 (1,2,4,9)	*b*
20	1,2,4,9	1,2,4,9 (1,2,4,6)	*b*
21	1,2,4,7	1,2,4,7 (1,2,4,8)	*c*
22	1,2,4,8	1,2,4,8 (1,2,4,7)	*c*

[a] Comparison with compound no. 2, 5, 7, 15, and 16 in isolated C–H out-of-plane bend region from 810 to 890 cm^{-1}. [b] Comparison with compound no. 9 and 11 in C–O–C asymmetric stretch region from 1280 to 1310 cm^{-1}. [c] Comparison with compound no. 17 and 18 in C–O–C asymmetric stretch region from 1260 to 1340 cm^{-1}.

create any ambiguity. It is easily shown that this ambiguity is completely removed by utilizing the 950–900 cm^{-1} bands.

The characteristic spectral region for distinguishing the individual TCDD isomers is from 1200 to 1600 cm^{-1}. This region contains the aromatic skeletal stretches, the C–O–C asymmetric stretches, and the C–H in-plane aromatic deformations which are sensitive to chlorine substitution in the TCDD structures. However, for certain isomers whose synthesis mode could lead to ambiguous products (compound no. 6, 8, and 10 to Table II), it was also necessary to compare the C–H out-of-plane region between 810 and 890 cm^{-1} with that of similarly substituted unambiguously prepared isomers. In this comparison particular emphasis was placed upon the isolated C–H out-of-plane benzene vibrations which should appear at the high end of this frequency range (*31*). The complete rationale for the assignment of structures to the 1,2,7,9 (compound 6), 1,2,6,8 (compound 8), and 1,2,7,8 (compound 10) is as follows: The 1,2,7,8 isomer has three peri hydrogens while the 1,2,7,9 and 1,2,6,8 isomers both have only two peri hydrogens. In addition the 1,2,7,8 isomer also has two pairs of vicinal chlorine substituents. Therefore one would expect the 1,2,7,9 and 1,2,6,8 spectra to be similar to each other and different from that of the 1,2,7,8 isomer. The spectra of compounds six and eight are similar since each contains five well-spaced bands in the 800–1000 cm^{-1} region, whereas compound 10 has one weak and two strong bands (one of which is an unresolved doublet near 800 cm^{-1}) in this region. Further proof that compound 10 is the 1,2,7,8 isomer comes from the observation of a very similar doublet at 800 cm^{-1} in the spectra of the 2,3,7,8 (compound 1), 1,4,7,8 (compound 5), and 1,3,7,8 (compound 2) isomers.

Compound 6 is assigned as the 1,2,7,9 isomer by comparison to the unambiguously assigned 1,3,7,9 isomer (compound 16) and is based on a better frequency correlation in the 800 cm^{-1} region (one of the strongest bands in the 1,3,7,9 spectrum). Similarly compound 8 is assigned as the 1,2,6,8 isomer based on the weaker intensity exhibited in the 800 cm^{-1} region which is also seen in the 1,3,6,8 isomer (compound 15). For those isomers whose structure was still ambiguous at this point (compound no. 19, 20, 21, and 22), it was also necessary to similarly compare the C–O–C asymmetric stretch region between 1280 and 1310 cm^{-1}, 1260 and 1310 cm^{-1}, and 1260 and 1340 cm^{-1} with the same frequency region of unambiguous isomers. The rationale for the tentative assignments of the uncertain isomers is summarized in the footnotes to Table II.

Although these structural assignments should not be considered unequivocal, currently available quantities of these isomers preclude confirmation by other spectral techniques such as Fourier transform nuclear magnetic resonance.

CONCLUSIONS

Micro-DRIFT sensitivity limits over 3 orders of magnitude better than those reported by Chen (*22*) for the 2,3,7,8-, 1,2,3,4-, and 1,3,6,8-TCDD isomers using micro-IR grating techniques have been achieved. The micro-DRIFT spectra prepared as a surface film on KBR pellets were qualitatively similar to the previously reported micrograting spectra which were measured from solid KBR pellets.

In contrast to DRIFT analysis, the 22 TCDD isomers cannot be distinguished from one another based on their mass spectra. Use of GC/MS in conjunction with chromatographic retention times does permit identification of a number of the isomers; however, coelution of one or more isomers still prohibits identification of all 22 compounds by this technique. Since the 22 TCDD FT-IR spectra are unique, chromatographic coelution of these isomers may be compensated for by FT-IR spectral subtraction. This technique has been successfully utilized to identify 2,3,7,8-TCDD in soil extracts in the presence of chromatographic interferences (*32*).

Registry No. 2,3,7,8-TCDD, 1746-01-6; 1,2,3,6-TCDD, 71669-25-5; 1,2,3,8-TCDD, 53555-02-5; 1,2,8,9-TCDD, 62470-54-6; 1,2,3,7-TCDD, 67028-18-6; 1,3,6,8-TCDD, 33423-92-6; 1,2,6,7-TCDD, 40581-90-6; 1,2,6,9-TCDD, 40581-91-7; 1,4,7,8-TCDD, 40581-94-0; 1,2,3,4-TCDD, 30746-58-8; 1,3,7,8-TCDD, 50585-46-1; 1,2,7,9-TCDD, 71669-23-3; 1,2,6,8-TCDD, 67323-56-2; 1,2,3,9-TCDD, 71669-26-6; 1,2,7,8-TCDD, 34816-53-0; 1,3,6,9-TCDD, 71669-24-4; 1,4,6,9-TCDD, 40581-93-9; 1,3,7,9-TCDD, 62470-53-5; 1,2,4,6-TCDD, 71669-27-7; 1,2,4,9-TCDD, 71665-99-1; 1,2,4,7-TCDD, 71669-28-8; 1,2,4,8-TCDD, 71669-29-9.

LITERATURE CITED

(1) Cairns, T.; Fishbein, L.; Mitchum, R. K. *Biomed. Mass Spectrom.* **1980**, *7*, 484.
(2) Mahle, N. H.; Shadoff, L. A. *Biomed. Mass Spectrom.* **1982**, *9*, 45.
(3) Hass, J. R.; Friesen, M. D. *N.Y. Acad. Sci.* **1979**, *320*, 28.
(4) McConnell, E. E.; Moore, J. A.; Haseman, J. K.; Harris, M. W. *Toxicol. Appl. Pharmacol.* **1978**, *44*, 335.
(5) di Domenico, A.; Merli, F.; Boniforti, L. *Anal. Chem.* **1979**, *51*, 735.
(6) Hummel, R. A.; Shadoff, L. A. *Anal. Chem.* **1980**, *52*, 191.
(7) Shadoff, L. A.; Hummel, R. A. *Biomed. Mass Spectrom.* **1978**, *5*, 7.
(8) Hass, J. R.; Friesen, M. D.; Harran, D. J.; Parker, C. E. *Anal. Chem.* **1978**, *50*, 1474.
(9) Crow, F. W.; Bjorseth, A.; Knapp, K. T.; Bennet, R. *Anal. Chem.* **1981**, *53*, 619.
(10) Buser, H. *Anal. Chem.* **1976**, *48*, 1553.
(11) Mitchum, R. K.; Moler, G. F.; Korfmacher, W. A. *Anal. Chem.* **1980**, *52*, 2278.
(12) Hunt, D. F.; Harvey, T. M.; Russel, J. W. *J. Chem. Soc., Chem. Commun.* **1975**, 151.
(13) Hass, J. R.; Friesen, M. D.; Hoffman, M. K. *Org. Mass Spectrom.* **1979**, *14*, 9.
(14) Buser, H. R.; Rappe, C. *Anal. Chem.* **1980**, *52*, 2257.
(15) Nestrick, T. J.; Lamparski, L. L.; Stehl, R. H. *Anal. Chem.* **1979**, *51*, 2273.
(16) Gurka, D. F.; Laska, P. R.; Titus, R. *J. Chromatogr. Sci.* **1982**, *20*, 145.
(17) Gurka, D. F.; Betowski, L. *Anal. Chem.* **1982**, *54*, 1819.
(18) Gurka, D. F.; Hiatt, M.; Titus, R. *Anal. Chem.* **1984**, *56*, 1102.
(19) Cournoyer, R.; Shearer, J. C.; Anderson, D. H. *Anal. Chem.* **1977**, *49*, 2275.
(20) Fuller, M. P.; Griffiths, P. R. *Appl. Spectrosc.* **1980**, *34*, 533.
(21) Fuller, M. P.; Griffiths, P. R. *Anal. Chem.* **1978**, *50*, 1906.
(22) Chen, J. T. *J. Assoc. Off. Anal. Chem.* **1973**, *56*, 962.
(23) Yeboah, S. A.; Wang, S.; Griffiths, P. R. *Appl. Spectrosc.* **1984**, *38*, 259.
(24) Hamadeh, I. M.; Yeboah, S. A.; Trumbull, K. A.; Griffiths, P. R. *Appl. Spectrosc.* **1984**, *38*, 486.
(25) Bracket, J. M.; Azarraga, L. V.; Castles, M. S. *Anal. Chem.* **1984**, *56*, 2007.
(26) Nyquist, R. A.; Putzig, C. L.; Peterson, D. P. *Appl. Spectrosc.* **1983**, *37*, 140.
(27) Kuehl, D. and Griffiths, P. R. *J. Chromatogr. Sci.* **1979**, *17*, 471.
(28) Griffiths, P. R.; Duff, P. J.; Azarraga, L. V. *Anal. Chem.* **1984**, *56*, 2636.
(29) Griffiths, P. R. and Shafer, K. H. Presented at the 11th Annual FACSS Meeting in Philadelphia, PA, Sept 19, 1984; Abs. 272.
(30) Shafer, K. H.; Pentoney, S. L., Jr.; Griffiths, P. R. *HRC CC, J. High Res. Chromatogr. Chromatogr. Commun.* **1984**, *7*, 707.

(31) Alpert, N. L.; W. E.; Syzmanski, H. A. "Theory and Practice of Infrared Spectroscopy", 2nd ed.; Plenum/Rosetta Press: New York, 1973; p 265.
(32) Gurka, D. F.; Billets, S.; Brasch, J.; Riggle, C. J.; Bourne, S., to be presented at the 1985 International Conference on Fourier and Computerized Infrared Spectroscopy in Ottawa, Canada, June 27, 1985.

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